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(54) Title: LEAD-FREE CRYSTAL GLASS

(57) Abstract

Crystal lead-free glass suitable for man-made and machine-made utility glass especially of luxurious character with a higher refractive index, containing in % by weight from 50 to 65 of silicon dioxide SiO_2, from 0.1 to 10 of aluminium oxide Al_2O_3, from 0.5 to 17 of zirconium dioxide ZrO_2, from 10 to 22 of potassium K_2O and/or sodium Na_2O oxide, from 2 to 10 of calcium CaO and/or magnesium MgO oxide, the content of ferric oxide Fe_2O_3 being within the range from 0.01 to 0.025 % by weight. The properties of said glass are modified at least by one oxide from the group comprising barium BaO, zinc ZnO, boron B_2O_3 and lithium Li_2O oxides. The further modifiers are either individually or in combination antimony trioxide Sb_2O_3, titanium dioxide TiO_2 and stannic dioxide SnO_2 within the range from a trace to 1 % by weight of antimony trioxide Sb_2O_3, titanium dioxide TiO_2 and stannic dioxide SnO_2.

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Lead-free crystal glass

Technical field

This invention relates to crystal lead-free glass which is intended especially for the man-made and machine-made utility glassware, with the refractive index within the range from 1,53 to 1,58. The glass contains silicon dioxide SiO_2, aluminium oxide Al_2O_3, zirconium dioxide ZrO_2, calcium CaO and/or magnesium MgO oxide, potassium K_2O and/or sodium Na_2O oxide.

Background art

The classification of crystal utility glass types according to ČSN 70 001 is as follows:

- crystal soda potash glass containing in total potassium K_2O and sodium Na_2O oxides $\geq$ 10 % by weight, the value of refractive index being not required
- crystal glass containing potassium K_2O, barium BaO and lead oxides in total $\geq$ 10 % by weight, with the refractive index of about 1,51
- special crystal glass containing potassium oxide K_2O, zirconium dioxide ZrO_2, barium BaO and lead oxides in total $\geq$ 10 % by weight, with the refractive index from 1,51 to 1,525
- lead crystal glass with the content of lead oxide $\geq$ 24 % by weight with the refractive index of $\geq$ 1,545
- high lead crystal glass with the content of lead oxide $\geq$ 30 % by weight with the refractive index >> 1,545.

Also, the crystal soda potash glass which is a czech speciality from the historical point of view. Remaining crystal glass types correspond to EC - directions. The first two crystal glass types mentioned above are being used for products from so called cheap crystal glass which are accented above all by a low price and refractive index ranges about the value of 1,51.

Barium BaO and lead oxides being used by some manufacturers and in smaller amounts only, as is stated e.g. by A. Smrček in the journal Sklář a keramik 38, /1988/, p. 286-294. The group of specialty crystal glass types represents more noble products in which the refractive index is observed to range about the value 1,52 and which is obtained by dosing of barium BaO and zinc ZnO oxides, alternatively also of lead oxide, as is specified e.g. in BRD-patent from 1987 No. 2839645, such a glass according to the said patent contains in % by weight as follows: silicon dioxide SiO_2 65 to 75, aluminium oxide Al_2O_3 0,1 to 2, calcium oxide CaO 2 to 12, magnesium oxide MgO 0 to 8, sodium oxide Na_2O 7 to 15, potassium oxide K_2O 0 to 10, lithium oxide Li_2O 0 to 3, barium oxide BaO 1 to 6, zinc oxide ZnO 0,2 to 3, lead oxide 0 to 10 and titanium dioxide TiO_2 0,2 to 5. This invention covers by its chemical composition, with the exception of titanium dioxide TiO_2, most of crystal glass types being produced excepting of lead and high-lead crystal glass types with the content of lead oxide $\geq$ 24 % by weight.

For the products of luxurious character which are decorated predominatingly by grinding the lead and high-lead crystal glass types are being used where the refractive index of $\geq$ 1,545 is required. At the present time the unharmful hygienic properties are being preferred particularly concerning the content of lead and barium in the leach. With regard to a fact that in the production of those special crystal glass types the refractive index of the desired value is being elevated largely by an increased amount of barium BaO and lead oxides, the said hygiene properties that are required induce insolvable problems in the production of such glass types.

Disclosure of the invention

According to this invention the disadvantages

mentioned above are removed or substantially reduced by using the crystal lead-free glass with the content of zirconium dioxide ZrO_2 which is characterized by the content from 50 to 65 % by weight of silicon dioxide SiO_2, from 0,1 to 10 % by weight of aluminium oxide Al_2O_3, from 0,5 to 17 % by weight of zirconium dioxide ZrO_2, from 10 to 22 % by weight of potassium K_2O and/or sodium Na_2O oxide, from 2 to 10 % by weight of calcium CaO and/or magnesium MgO oxide, the total amount of iron Fe expressed as iron trioxide Fe_2O_3 (ferric oxide) being ranged from 0,01 to 0,025 % by weight.

The functional and technological properties are with advantage modified by using at least one oxide from the group containing barium BaO, zinc ZnO, boron B_2O_3 and lithium Li_2O oxides amounted from 0,1 to 10 % by weight of barium BaO, zinc ZnO, boron B_2O_3 and lithium Li_2O oxides.

This glass type can with advantage contain traces to 1 % by weight of antimony trioxide Sb_2O_3, titanium dioxide TiO_2 and stannic dioxide SnO_2 either separately or in combination as further modifiers.

The advantage of said glass type is the decorative cutting and engraving ability comparable with the lead crystal glass, while having no content of lead oxide which is unhealthy and environmentally harmful. During melting of said glass type there does not occur the volatilization of environmentally harmful lead oxides and arsenic that are used in the manufacture of lead crystal glass. Thus, as the lead-free glass type is preferred which is intended especially for the utility glass, i.e. also for beverage packing glass and domestic glass, it features the advantage of undesirable and unhealthy lead oxide being not penetrated into the leach. The melting and refining of said molten glass types is easier when compared with lead crystal molten glass types as the lead-free glass types feature lower melting temperatures.

Especially, the melting temperature and the

temperature point of liquidus are improved by addition of modifying additives, namely of barium BaO, zinc ZnO, boron B_2O_3 and lithium Li_2O oxides. Moreover, said oxides positively affect the refractive index of glass.

The antimony trioxide Sb_2O_3 is used for the refining ability to be improved. Both titanium dioxide TiO_2 and stannic oxide SnO including antimony trioxide Sb_2O_3 also increase the value of the refractive index.

Examples of carrying out invention

The invention will be further described, by way of the following examples of carrying out.

Example No.	1	2	3	4
Glass component	content in % by weight			
Silicium dioxide SiO_2	60,68	58,31	61,75	60,77
Aluminium oxide Al_2O_3	5,00	0,38	5,00	5,00
Zirconium dioxide ZrO_2	8,3	14,9	3,5	3,5
Calcium oxide CaO	6,00	5,58	5,40	5,40
Magnesium oxide MgO	0,00	0,40	0,00	0,00
Sodium oxide Na_2O	12,00	19,87	7,00	8,00
Potassium oxide K_2O	8,00	0,25	6,00	6,00
Barium oxide B_2O_3	0,00	0,00	9,00	0,00
Zinc oxide ZnO	0,00	0,00	0,00	9,00
Lithium oxide Li_2O	0,00	0,00	0,00	2,00
Antimony trioxide Sb_2O_3	0,00	0,29	0,33	0,32
Iron content expressed by amount of iron trioxide	0,015	0,02	0,02	0,01
Total oxides	100,00	100,00	100,00	100,00
$t_{\log \eta=2}$ [°C]	1504	1405	1430	1408
$t_{\log \eta=4}$ [°C]	1114	1087	1012	1008
$t_{\log \eta=7,65}$ [°C]	827	844	714	721
$t_{\log \eta=13}$ [°C]	637	678	523	535
$t_{\log \eta=14,5}$ [°C]	602	647	489	501
$t_{liquidus}$ [°C]	963	1210	930	950
refractive index at 589,3 [nm]	1,545	1,572	1,542	1,543
density at 20 °C [$g.cm^{-3}$]	2,628	2,754	2,685	2,683
$\alpha_{20-300°C} \cdot 10^6$ [$°C^{-1}$]	9,16	9,37	8,80	8,82
grindability [$\mu m.min^{-1}$]	0,312	0,343	0,329	0,372

Example No.	5	6	7
Glass components	content in % by weight		
Silicium dioxide SiO_2	60,37	60,17	66,07
Aluminium oxide Al_2O_3	7,00	5,00	0,00
Zirconium dioxide ZrO_2	6,30	8,30	5,00
Calcium oxide CaO	6,00	6,00	5,40
Sodium oxide Na_2O	10,00	10,00	6,00
Potassium oxide K_2O	8,00	8,00	6,00
Lithium oxide Li_2O	2,00	0,00	2,00
Barium oxide BaO	0,00	0,00	6,00
Zinc oxide ZnO	0,00	0,00	3,00
Boron oxide B_2O_3	0,00	2,00	0,00
Antimony trioxide Sb_2O_3	0,31	0,32	0,31
Titanium dioxide TiO_2	0,00	0,20	0,00
Stannic dioxide SnO_2	0,00	0,00	0,20
Iron content expressed by amount of iron trioxide	0,02	0,01	0,02
Total oxides	100,00	100,00	100,00
$t_{\log \eta=2}$ [°C]	1425	1518	1470
$t_{\log \eta=4}$ [°C]	1027	1112	1040
$t_{\log \eta=7,65}$ [°C]	739	815	738
$t_{\log \eta=13}$ [°C]	552	621	539
$t_{\log \eta=14,5}$ [°C]	518	556	503
$t_{liquidus}$ [°C]	970	950	844
refractive index at 589,3 [nm]	1,543	1,545	1,544
density at 20 °C [$g.cm^{-3}$]	2,5909	2,6206	2,6748
$\alpha_{20-300°C} \cdot 10^6$ [$°C^{-1}$]	8,90	7,93	8,68
grindability [$\mu m.min^{-1}$]	0,279	0,192	0,185

In the presented examples corresponds $t_{\log \eta=2}$ to the temperature of glass melting, $t_{\log \eta=4}$ to the temperature of glass forming, $t_{\log \eta=7,65}$ to the temperature of Littleton point of glass softening, $t_{\log \eta=13}$ to the upper annealing temperature and $t_{\log \eta=14.5}$ to the lower annealing temperature and $\alpha_{20-300°C}$ to the mean coefficient of thermal expansivity of glass in the range from 20 to 300 °C. The grindability is expressed by a loss of sample weight in $\mu m.min^{-1}$ onto a diamond grinding wheel with the dimensions of grain 120 μm under loading of 1,71 $g.mm^{-2}$

The melting temperature that corresponds to the molten glass viscosity of log η = 2 is approximately 1500 °C for the lead glass types. For glass types according to this invention is either comparable with lead glass types or e.g. in accordance with the examples No. 1 and No. 6 or lowered by 30 °C for the molten glass type according to the example No. 7, by 75 °C for the molten glass according to the example No. 5, by 92 °C for the molten glass according to the example No. 4, by 70 °C for the molten glass according to the example No. 3 and by 95 °C for the molten glass according to the example No. 2.

All temperatures of point of liquidus except of the composition No. 2 that is characterized by a high content of zirconium dioxide, are lower than the forming temperatures corresponding to the temperature at a viscosity of molten glass log η = 4 so that with these molten glass types the tendency to undesirable crystallization is restrained.

For the lead crystal the refractive index is approximately 1,545, for the glass types according to this invention it ranges within 1,542 and 1,572. Thus, the optical properties of final products are comparable or better ones when comparing with products made of lead crystal glass which will especially reflect on decorative cut and engraved products.

The mean coefficient of linear thermal expansivity α within range from 20 to 300 °C is in all cases lower than for so far used crystal glass types in general which is favourable for the resistance of glass against the thermal shock.

The grindability for the lead crystal glass is according to the chosen method 0,266 $\mu m.min^{-1}$ and for embodiments according to the composition No. 1 to No. 5 it is higher which will favourable affect the velocity of processing of these glass types by means of decorative cutting and engraving.

Industrial applicability

The lead-free crystal glass according to this invention with the content of zirconium dioxide ZrO_2 is intended for man-made and machine-made utility glassware with a higher refractive index, it is suitable particularly for glass decorated by cutting and engraving and by further decorative techniques for products of the luxurious character. This glass type is hygienic unharmful concerning the content of detrimental substances in the leach and by its brilliance can compete with the products made of lead crystal glass.

The question there is both the production of glass objects used in households and restaurants, e.g. small cups, tumblers, carafes, bowls and vessels of various shapes and sizes used for decorative purposes, such as vases, dishes etc.

Claims

1. Crystal lead-free glass suitable especially for man-made and machine-made utility glass with the refractive index within the range from 1,53 to 1,58, containing silicon dioxide SiO_2, aluminium oxide Al_2O_3, zirconium dioxide ZrO_2, calcium CaO and/or magnesium MgO oxide, potassium K_2O and or sodium Na_2O oxide, characterized by its composition, with the content of 50 to 65 % by weight of silicon dioxide SiO_2, 0.1 to 10 % by weight of aluminium oxide Al_2O_3, 0,5 to 17 % by weight of zirconium dioxide ZrO_2, 10 to 22 % by weight of potassium K_2O and/or sodium Na_2O oxide, 2 to 10 % by weight of calcium CaO and/or magnesium MgO oxide, the content of ferric oxide Fe_2O_3 being within the range from 0,01 to 0,025 % by weight.

2. Crystal lead-free glass according to claim 1, characterized by its composition, with the range from 0,1 to 10 % by weight of barium oxide BaO, zinc oxide ZnO, boron trioxide B_2O_3 and lithium oxide Li_2O.

3. Crystal lead-free glass according to claims 1 and 2, characterized by its composition, with the content, individually or in a combination, of the traces to 1% by weight of antimony trioxide Sb_2O_3, titanium dioxide TiO_2 and stannic dioxide SnO_2.

INTERNATIONAL SEARCH REPORT

PCT/CS 92/00012

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C03C3/087; C03C3/093

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C03C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	CHEMICAL ABSTRACTS, vol. 109, no. 16, 9 October 1988, Columbus, Ohio, US; abstract no. 133790Y, page 292 ; see abstract & JP,A,63 147 843 (NIPPON SHEET GLASS CO) 20 June 1988	1-3
Y	EP,A,0 405 579 (KIRIN BEER K.K.) 2 January 1991 see page 3, line 24 - page 5, line 14	1-3
Y	US,A,4 065 317 (BAAK) 27 December 1977 see column 3, line 19 - line 32; claims see column 11, line 26 - line 31	1-3

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IV. CERTIFICATION

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	CHEMICAL ABSTRACTS, vol. 85, no. 8, 23 August 1976, Columbus, Ohio, US; abstract no. 50963S, page 282 ; see abstract & JP,A,51 055 310 (SUWA SEIKOSHA CO.) 15 May 1976 ---	1-3
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. CS 9200012 SA 58812

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP-A-63147843	20-06-88	None	
EP-A-0405579	02-01-91	JP-A- 3037131	18-02-91
US-A-4065317	27-12-77	None	
JP-A-51055310	15-05-76	None	
JP-A-61270234	29-11-86	None	